8 Superposition of states and their time evolution

8.1 Superposition of states

Quantum mechanics postulates that if we have some generic state $\phi(x)$ that is not an eigenstate of the Hamiltonian, we can always represent is as a combination of eigenstates of the Hamiltonian operator $\hat{H}$, $\psi_n(x)$.[1] For example, in the case of the particle in a box we can write

[1]We can actually use eigenstates of any Hermitian operator, e.g., $\hat{p}$.

$$\phi(x) = \sum_{n=0}^{\infty} c_n \psi_n(x) = \sum_{n=0}^{\infty} c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \tag{1}$$

where the numbers c_n are complex and are often referred to as expansion coefficients or just coefficients. These coefficients must have norm less or equal to one

$$|c_n|^2 \leq 1 \quad \forall n, \tag{2}$$

and their sum must be equal to one

$$\sum_{n=0}^{\infty} |c_n|^2 = 1. \tag{3}$$

Quantum mechanics tells us that when we measure the energy of state $\phi(x)$ we will get as a result one of the eigenvalues of the Hamiltonian. However, if we know the expansion coefficients of $\phi(x)$ we can say something more. Indeed, the probability of measuring the energy E_n is equal to the modulus square of the coefficient for eigenstate $\psi_n(x)$

$$\text{Probability of measuring } E_n = P_n = |c_n|^2. \tag{4}$$

For example, consider the state

$$\phi(x) = \underbrace{\frac{1}{\sqrt{2}}}_{c_1} \psi_1(x) \underbrace{-i\frac{1}{\sqrt{2}}}_{c_3} \psi_3(x). \tag{5}$$

Here we can immediately identify the coefficient for each state. We have $c_1 = \frac{1}{\sqrt{2}}$ and $c_3 = -i\frac{1}{\sqrt{2}}$, and all other coefficients are zero, $c_2 = c_4 = \ldots = 0$. What is the probability of measuring E_1 and E_3? We can compute these quantities by taking the square of the wave function coefficients

$$\begin{aligned} P_1 &= \left|\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2}, \\ P_3 &= \left|-i\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2}. \end{aligned} \tag{6}$$

This result generalizes to any Hermitian operator $\hat{A}$. Suppose we know the eigenfunctions of $\hat{A}$, $\psi_n(x)$, and the corresponding eigenvalues a_n

$$\hat{A}f_n(x) = a_n f_n(x), \tag{7}$$

then a generic wave function $\phi(x)$ may be expanded as

$$\phi(x) = \sum_{n=0}^{\infty} c_n f_n(x), \tag{8}$$

and the probability that a measurement of $\hat{A}$ gives the value a_n is given by

$$\text{Probability of measuring } a_n = P_n = |c_n|^2. \tag{9}$$

What happens after a measurement? A measurement changes the wave function of a system so if we measure the final state and obtain the value a_n the state is in the eigenstate $f_n(x)$. If a measurement is then repeated we will continue to obtain the same value, a_n, and the system will be in the same state, $f_n(x)$,

$$\phi(x) \xrightarrow{\text{Measurement of } \hat{A}} f_n(x) \xrightarrow{\text{Measurement of } \hat{A}} f_n(x) \tag{10}$$

This phenomenon is called the **collapse of the wave function**. This is perhaps one of the most puzzling aspects of quantum mechanics and it is the source of paradoxes like the one involving Schrödinger's cat (**click here for a link to video**).

8.2 Evaluation of the expansion coefficients

Suppose the we know a generic state $\phi(x)$ but we do not know the expansion coefficients c_n, how can we determine them? Recall that here we assumed that the operator $\hat{A}$ is Hermitian, and that the eigenfunctions of Hermitian operators are orthonormal. Let us compute the integral of $\phi(x)$ with the complex conjugate of one of the eigenfunctions of $\hat{A}$, say $f_k(x)$

$$
\begin{aligned}
\int f_k^*(x)\phi(x)\,dx &= \int f_k^*(x) \sum_{n=0}^{\infty} c_n f_n(x)\,dx \\
&= \sum_{n=0}^{\infty} c_n \underbrace{\int f_k^*(x) f_n(x)\,dx}_{\delta_{kn}} \\
&= \sum_{n=0}^{\infty} c_n \delta_{kn} = c_k.
\end{aligned}
\tag{11}
$$

Here we used the Kronecker delta (δ_{in}), defined as

$$
\delta_{kn} = \begin{cases} 1 & \text{if } k = n \\ 0 & \text{if } k \neq n. \end{cases}
\tag{12}
$$

When we write

$$\int f_k^*(x) f_n(x)\,dx = \delta_{kn}, \tag{13}$$

we are condensing both the normalization (when $k = n$) and the orthogonality (when $k \neq n$) conditions of the functions $f_n(x)$ in one line.

Going back to our integral, we find that the expansion coefficients may be determined as

$$c_k = \int f_k^*(x)\phi(x)\,dx = \langle f_k | \phi \rangle. \tag{14}$$

Here we introduced the bra–ket notation[2] for the integral ($\langle \cdot | \cdot \rangle$), which, for a pair of generic functions $f(x)$ and $g(x)$ is defined as

$$\langle f | g \rangle = \int f^*(x) g(x)\,dx. \tag{15}$$

[2]This notation was introduced by physicist Paul Dirac and is also known as Dirac notation.

Going back to the analogy of functions and vectors, the quantity $\langle f | g \rangle$, which is called the inner product of $f(x)$ and $g(x)$, may be considered the function analog of the dot product for vectors.

8.3 Expectation values of general wave functions

Next, we want to understand how to relate the expectation value of a superposition of state to that of the individual eigenstates used to expand it. We will start with a special case and consider the expectation value of the energy for a wave function expanded in the energy eigenstates. The expectation value of the energy is given by

$$\langle \hat{H} \rangle = \int \phi^*(x) \hat{H} \phi(x)\, dx = \langle \phi | \hat{H} | \phi \rangle. \tag{16}$$

To evaluate this quantity we expand $\phi(x)$ using Eq. (1) to get

$$\langle \hat{H} \rangle = \int \left[\sum_{m=0}^{\infty} c_m \psi_m(x) \right]^* \hat{H} \left[\sum_{n=0}^{\infty} c_n \psi_n(x) \right] dx = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n \int \psi_m^*(x) \hat{H} \psi_n(x)\, dx. \tag{17}$$

Note that since $\psi_n(x)$ is an eigenfunction of $\hat{H}$ we can simplify the integral

$$\int \psi_m^*(x) \hat{H} \psi_n(x)\, dx = \int \psi_m^*(x) E_n \psi_n(x)\, dx = E_n \int \psi_m^*(x) \psi_n(x)\, dx = E_n \delta_{mn}. \tag{18}$$

If we plug this result back into the expression for the expectation value of the energy we get

$$\langle \hat{H} \rangle = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n E_n \delta_{mn} = \sum_{n=0}^{\infty} c_n^* c_n E_n = \sum_{n=0}^{\infty} |c_n|^2 E_n. \tag{19}$$

This result tells us that the average energy is a weighted average of the energy of all states, where the weight of a state is given by the square of the coefficient $|c_n|^2$.

For a general operator $\hat{A}$ we derive the more general result

$$\langle \hat{A} \rangle = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* c_n \int \psi_m^*(x) \hat{A} \psi_n(x)\, dx, \tag{20}$$

which depends on the value of the integral

$$A_{mn} = \int \psi_m^*(x) \hat{A} \psi_n(x)\, dx = \langle \psi_m | \hat{A} | \psi_n \rangle. \tag{21}$$

In general we cannot simplify this integral and we have to evaluate it either using analytic or numerical integration. The notation used in Eq. (21) suggest thinking of A_{mn} as a matrix[3] (**A**), which allows us to rewrite the expectation value as[4]

$$\langle \hat{A} \rangle = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} c_m^* A_{mn} c_n. \tag{22}$$

8.4 Time evolution of general wave functions

In general, a superposition of state is not stationary, that is, it will evolve over time. In this section we will study how a generic wave function evolves over time. Let us assume that at $t = 0$ the wave function is a superposition of energy eigenstates with coefficients c_n

$$\phi(x, t = 0) = \sum_{n=0}^{\infty} c_n \psi_n(x). \tag{23}$$

At a later time, $t > 0$, the wave function will change, but we can still represent it as a linear combination of energy eigenstates, except for the fact that the coefficients will be different. If we indicate the coefficients at time t as $c_n(t)$ the wave function is then given by

$$\phi(x, t) = \sum_{n=0}^{\infty} c_n(t) \psi_n(x). \tag{24}$$

[3] A matrix is just a table of numbers with indices that represent the coordinates of the entries.

[4] Is it possible to write this term also as a quadratic form, $\langle \hat{A} \rangle = \mathbf{c}^\dagger \mathbf{A} \mathbf{c}$, where $\mathbf{c}$ stands for the vector c_n and the dagger symbol $\dagger$ indicates the Hermitian adjoint.

To find the coefficients $c_n(t)$ we plug this equation into the time-dependent Schrödinger equation to get

$$i\hbar \frac{\partial}{\partial t} \sum_{n=0}^{\infty} c_n(t)\psi_n(x) = \hat{H} \sum_{n=0}^{\infty} c_n(t)\psi_n(x), \tag{25}$$

taking the derivate with respect to time on the l.h.s. and applying the Hamiltonian operator on the r.h.s. we arrive at

$$i\hbar \sum_{n=0}^{\infty} \frac{\partial c_n(t)}{\partial t}\psi_n(x) = \sum_{n=0}^{\infty} c_n(t)\hat{H}\psi_n(x) = \sum_{n=0}^{\infty} c_n(t)E_n\psi_n(x). \tag{26}$$

Now we use a trick that we will encounter many times: multiply both sides with $\psi_k^*(x)$ and integrate

$$i\hbar \sum_{n=0}^{\infty} \frac{\partial c_n(t)}{\partial t} \int \psi_k^*(x)\psi_n(x)\, dx = \sum_{n=0}^{\infty} c_n(t)E_n \underbrace{\int \psi_k^*(x)\psi_n(x)\, dx}_{\delta_{kn}}. \tag{27}$$

The quantities inside the integral are Kronecker deltas (see Sec. 8.2), and are equal to one only if $k = n$. This leads to the much simpler equation

$$i\hbar \frac{\partial c_k(t)}{\partial t} = c_k(t)E_k. \tag{28}$$

We have already solved this equation when we introduced the time-dependent Schrödinger equation. The solution is

$$c_n(t) = c_n e^{-iE_n t/\hbar}, \tag{29}$$

where we used the initial condition $c_n(0) = c_n$. Plugging this result in Eq. (24) we arrive at the general solution of the time-dependent Schrödinger equation

$$\phi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}. \tag{30}$$

Note that this result is only valid if E_n and $\psi_n(x)$ are eigenvalue/eigenfunction of the Hamiltonian operator.

Exercise 8.1 Consider a wave function that at time $t = 0$ is equal to the superposition of states

$$\phi(x,0) = \frac{1}{\sqrt{2}}\psi_1(x) - \frac{1}{\sqrt{2}}\psi_2(x). \tag{31}$$

Show that the solution to the time-dependent Schrödinger equation is given by

$$\phi(x,t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1 t/\hbar} - \frac{1}{\sqrt{2}}\psi_2(x)e^{-iE_2 t/\hbar}, \tag{32}$$

by plugging in this function in the time-dependent Schrödinger and verifying that the l.h.s. equals the r.h.s. ∎

Exercise 8.2 Compute the probability density $[\rho(x,t)]$ of the time-dependent wave function

$$\phi(x,t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}}\psi_2(x)e^{-iE_2 t/\hbar} \tag{33}$$

expressing the time dependence in terms of trigonometric functions (sin / cos). Relate
the frequency of the time-dependent part of $\rho(x,t)$ to the energies E_1 and E_2. ∎